

Optoelectronic properties of PSS/oxidized carbon nanohorns composite films

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Abstract

Poly (styrene sulfonate) (PSS) / oxidized carbon nanohorns (CNHoxs) composite films were prepared and its optoelectronic properties were investigated. Majority carriers are turned out to be positive holes by Seebeck effect measurement. A heterojunction between PSS/CNHoxs and ZnO:Al showed rectifying behavior with a current rectification ratio of 10^4 . The PSS/CNHoxs films showed a significant transient response for IR light pulse. An IR-induced voltage at a junction between PSS/CNHs and ITO was observed obviously.

1. Introduction

Carbon-based nanomaterials such as carbon nanotube (CNT) and graphene have attracted attention due to its unique physical and chemical properties. Recently, broadband light detector [1] and terahertz scanner [2] were fabricated using CNT. Carbon nanohorn (CNH) which was discovered by Iijima et al. in 1999 [3], are derivative from single-walled CNT (SWCNT) with a horn-like structure. CNHs form a spherical aggregates with a diameter of 100 nm. Since CNHs absorb infrared (IR) light and transform it to heat effectively and include no metallic impurities, some biomedical application have been studied [4]. Further, photoelectrochemical sensors have been fabricated using CNHs [5]. While SWCNT has low dispersibility in solvents, CNHs aggregates are well dispersed in various organic solvents. Hole-opened CNHs (CNHoxs) obtained by oxidation treatment are dispersible even in water [6]. Therefore, large scale CNHoxs based devices could be fabricated with coating technique. In this work, we have studied optoelectronic properties, especially IR response of CNHoxs dispersed in poly (styrene sulfonate) (PSS) matrix.

2. Experimental

In this work, we used CNHoxs due to its dispersibility in water. Mixture of PSS (20 wt%) aqueous dispersion and 5 wt% CNHoxs suspension were coated by drop casting on glass substrates and dried in air. Film thickness was estimated to be $150 \mu\text{m}$. Aluminum doped ZnO (AZO) thin films were formed by a sol-gel technique on quartz substrate. We found that poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and carbon paste form Ohmic contacts for the

PSS/CNHoxs films and adopted them as electrodes. A heterojunction between PSS/CNHoxs and AZO was formed by direct bonding technique at a constant pressure of 0.5 kgf/cm^2 . We also formed PSS/CNHoxs films on an Indium Tin Oxide (ITO) substrates to fabricate a Schottky junction between PSS/CNHoxs and ITO. Current-voltage (I-V) characteristics of these junctions were investigated at room temperature. IR response measurement was carried out by irradiating IR laser pulse to ITO transparent electrode as shown in Fig. 1. Nd:YAG laser was used as a light source. The duration and energy of IR pulse were 10 ns and 0.3 mJ, respectively. Transient signals of IR response that appeared across an external resistance of $820 \text{ k}\Omega$ were measured by a digital storage oscilloscope (DSO6012A, Agilent Technologies). Seebeck effect measurement was carried out at room temperature using a thermoelectric property measurement system (RZ2001i, Ozawa Science, Japan).

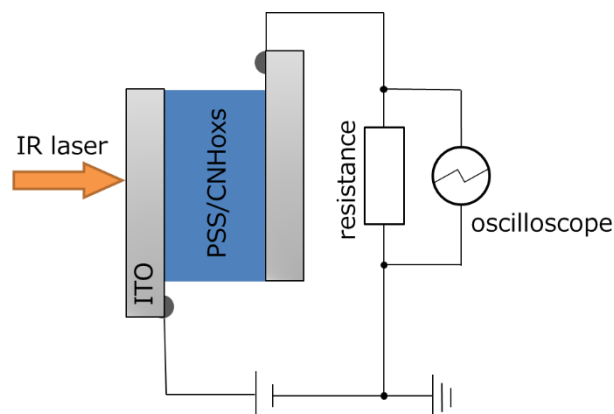


Fig. 1. Schematic diagram of IR response measurement.

3. Results and Discussion

Figure 2 shows I-V characteristics of the heterojunction between PSS/CNHoxs and AZO. Remarkable rectifying behaviors were observed both when PEDOT:PSS and carbon paste were used as electrodes for PSS/CNHoxs. The rectification ratio at 5 V for PEDOT:PSS and carbon paste electrodes are as high as 10^4 and 10^3 , respectively. The ideality factors are estimated to be 2.55 and 10.3, respectively. Nakano et al. have fabricated high quality Schottky junctions between PEDOT:PSS and ZnO single crystal [7]. In this work,

we succeeded in fabricating the IR absorbable rectifying contact using PSS/CNHoxs.

Figure 3 indicates I-V characteristics of the heterojunction between PSS/CNHoxs and ITO. We can recognize a significant rectifying behaviors. We studied IR response using this junction.

Figure 4 shows transient signal of the junction between PSS/CNHoxs and ITO for IR laser pulse at various negative bias voltages. It is found that peak intensity of transient signal increases with bias voltage. We should note that significant voltage with relaxation time longer than 50 ms can be observed even for zero bias. This may be due to photovoltaic effect. Seebeck coefficient of CNHoxs film was positive and its value was estimated to be $45 \mu\text{V/K}$. Majority carrier are turned out to be positive holes. Therefore, IR response at zero bias is ascribable to photo-thermoelectric (PTE) effect [8] or photo-Dember effect [9]. In Fig. 4, we also recognize that relaxation time decreases with bias voltage. It is plausible that this is attributed to change of carrier transit time between electrodes with bias voltage.

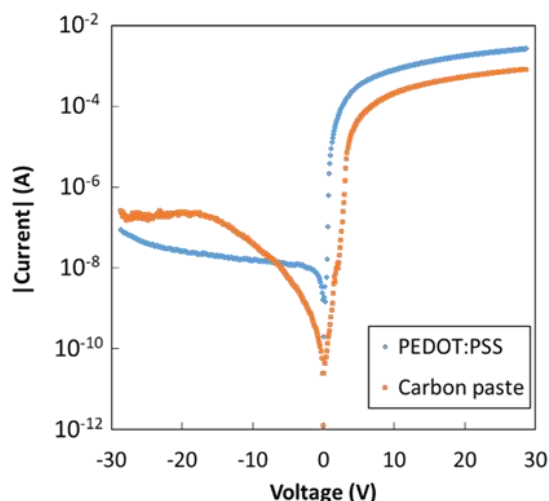


Fig. 2. I-V characteristics of the heterojunction between PSS/CNHoxs and AZO using PEDOT:PSS (blue) and carbon paste (red) as electrodes for PSS/CNHoxs.

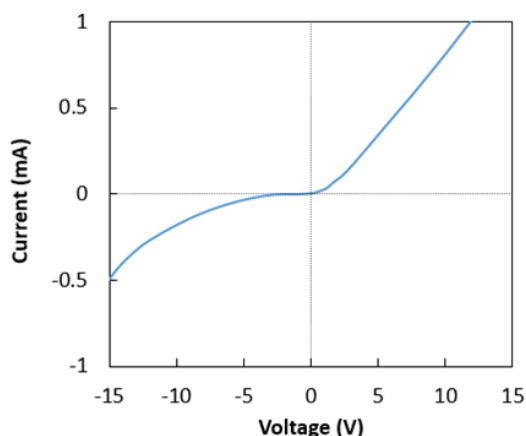


Fig. 3. I-V characteristics of the heterojunction between PSS/CNHoxs and ITO.

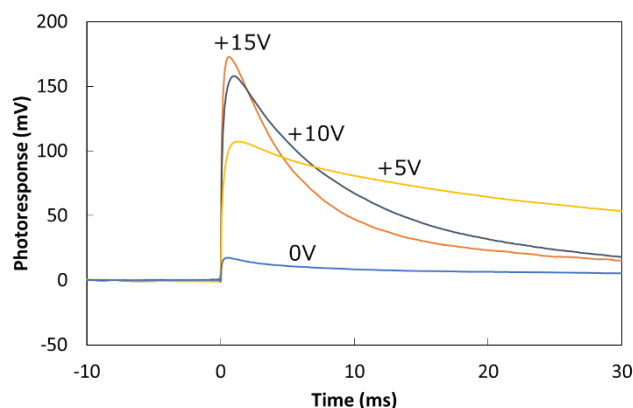


Fig. 4. Transient signal of the junction between PSS/CNHoxs and ITO for IR laser pulse at various bias voltages.

4. Conclusions

PSS/CNHoxs composite films were prepared by drop casting and its optoelectronic properties were studied. Significant rectifying behaviors were observed for the junction between PSS/CNHoxs and AZO formed by direct bonding. Transient IR response at the junction between PSS/CNHoxs and ITO was clearly observed even for zero bias.

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References

- [1] B. C. St-Antoine, D. Ménard and R. Martel, *Nano Lett.* **11** (2011) 609.
- [2] D. Suzuki, S. Oda and Y. Kawano, *Nat. Photonics* **10** (2016) 809.
- [3] S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai and K. Takahashi, *Chem. Phys. Lett.* **309** (1999) 165.
- [4] E. Miyako *et al.*, *Proc Natl Acad Sci USA* **109** (2012) 7523.
- [5] H. Dai, Y. Li, S. Zhang, L. Gong, X. Li and Y. Lin, *Sens. Actuators B* **222** (2016) 120.
- [6] S. Utsumi *et al.*, *J. Phys. Chem. B* **109** (2005) 14319.
- [7] M. Nakano, A. Tsukazaki, R. Y. Gunji, K. Ueno, A. Ohtomo, T. Fukumura and M. Kawasaki, *Appl. Phys. Lett.* **91** (2007) 142113.
- [8] X. Xu, N. M. Gabor, J. S. Alden, A. M. van der Zande and P. L. McEuen, *Nano Lett.* **10** (2010) 562.
- [9] V. Apostolopoulos and M. E. Barnes, *J. Phys. D* **47** (2014) 374002.